

OCTOBER 1991

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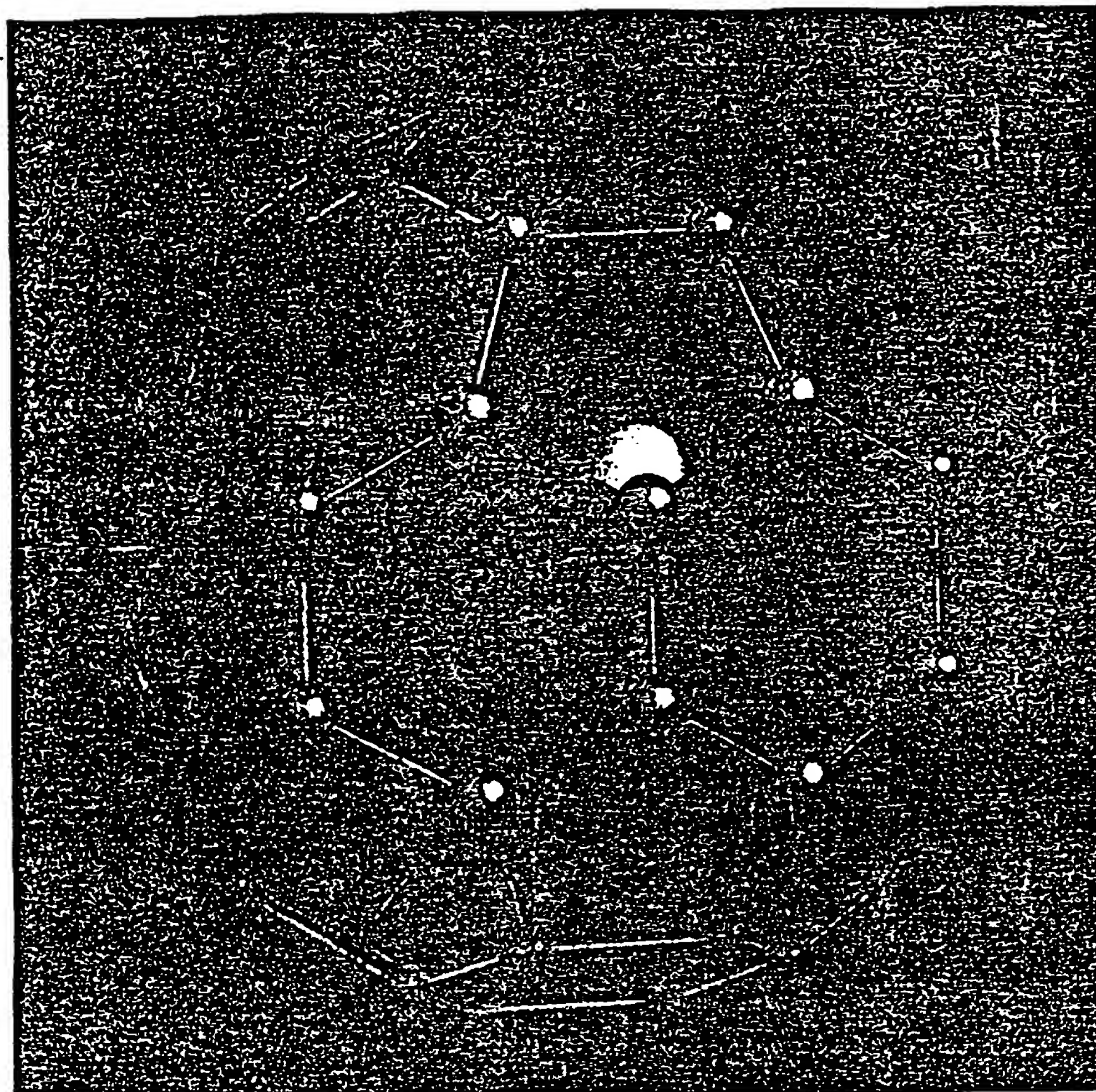
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# SCIENTIFIC AMERICAN

*Remnants of a planet that failed to form.*

*Still no technological fix for oil spills.*

*What made higher life-forms possible?*



*Buckyball, the third form of pure carbon, cages an atom in its lattice.*

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# Fullerenes

*These cage-like molecules constitute the third form of pure carbon (the other two are diamond and graphite). C<sub>60</sub>, the archetype, is the roundest molecule that can possibly exist*

by Robert F. Curl and Richard E. Smalley

In May of 1990 Wolfgang Krätschmer and his student Konstantinos Fostiropoulos carefully mixed a few drops of benzene with a specially prepared carbon soot. The clear solvent turned red.

Excitedly, the two workers for the Max Planck Institute for Nuclear Physics in Heidelberg telephoned their collaborators, Donald Huffman and Lowell Lamb of the University of Arizona in Tucson, who quickly repeated the experiment. The excitement continued as the two groups communicated daily by telephone and fax, exchanging measurements of the material—its infrared and ultraviolet spectra, its X-ray diffraction pattern and its mass spectrograph. Yes, the values all matched those predicted for the 60-atom carbon cluster buckminsterfullerene.

Even though some theorists had argued that this hollow, soccerball-shaped molecule should be detectable in abundance in such everyday circumstances as a candle flame, the German-American team had actually found it, succeeding where all others had failed. They were the first to observe this roundest of all round molecules, and they knew that chemistry books and encyclopedias would never be quite the same. Now there were three known forms of pure carbon: the network solids, diamond and graphite, and a new class of discrete molecules—the fullerenes.

When we heard of this breakthrough a few months later in Texas, we cele-

brated, with champagne all around. For although we had to some extent been scooped, we had been vindicated as well. Five years earlier we had had our own Eureka! experience. Together with our colleague Harold W. Kroto of the University of Sussex and our students James R. Heath and Sean C. O'Brien, we had found that C<sub>60</sub> could be made in a uniquely stable form simply by laser-vaporizing graphite in a pulsed jet of helium. We had gone on to propose that this extraordinary stability could be explained by a molecular structure having the perfect symmetry of a soccerball. Because the architectural principle also underlies the geodesic dome invented by the American engineer and philosopher R. Buckminster Fuller, we named it buckminsterfullerene, or buckyball for short.

In addition to C<sub>60</sub>, another molecule, C<sub>70</sub>, appeared to be quite special in these early experiments. We soon found that the stability of C<sub>70</sub> could be understood if the molecule had also taken the form of a geodesic dome. As Fuller had pointed out, all such domes can be considered networks of pentagons and hexagons. The 18th-century Swiss mathematician Leonhard Euler calculated that any such object must have precisely 12 pentagons in order to close into a spheroid, although the number of hexagons can vary widely. The soccerball structure of C<sub>60</sub> has 20 hexagons, whereas the structure we proposed for C<sub>70</sub> has 25, producing a shape reminiscent of a rugby ball.

In fact, we had found that all the even-numbered carbon clusters greater than about 32 atoms in size were remarkably stable (although less so than 60 or 70), and the evidence soon led us to postulate that all these molecules had taken the structure of geodesic domes. Again, in honor of Fuller, it seemed fitting to term this entirely new class of molecules the "fullerenes."

We later learned that such molecules had already been imagined. David E. H. Jones, writing under the pseudonym

"Daedalus" in the *New Scientist* in 1966, had conceived of a "hollow molecule" made of curled-up graphitic sheets. Others had predicted the stability of C<sub>60</sub> from calculations and tried—unsuccessfully—to synthesize it. We, however, were apparently the first to discover that the material could form spontaneously in a condensing carbon vapor.

Although our evidence was sound and our conclusions were supported by extensive further experiments and theoretical calculations, we could not collect more than a few tens of thousands of these special new molecules. This amount was plenty to detect and probe with the sophisticated techniques available in our laboratory, but there was not enough to see, touch or smell. Our evidence was indirect, much as it is for physicists who study antimatter. For now, the fullerenes existed only as fleeting signals detected in our exotic machines. But as chemists, we knew that the new material ought to be perfectly stable. Unlike antimatter, the geodesic forms of carbon should be quite safe to hold in one's bare hand. All we had to do was make more of them—billions and billions more.

Thus, for five years, we had been searching for a method of producing visible amounts of the stuff. We called our efforts "the search for the yellow vial" because quantum calculations for such a soccerball-shaped carbon molecule suggested it would absorb light strongly only in the far violet part of the spectrum. We were not alone. Our initial "soccerball"

**HYPERFULLERENE STRUCTURE** called a Russian egg is expected to form along with ordinary fullerenes in a laser-vaporized carbon plume. Shown here is the most symmetric form: a C<sub>50</sub> at the core is encapsulated by fullerenes having 240, 540 and 960 atoms. This process could continue indefinitely to produce a macroscopic particle whose pentagons are in icosahedral alignment.

ROBERT F. CURL and RICHARD E. SMALLEY of Rice University have collaborated for the past seven years in research on carbon and semiconductor clusters in supersonic beams. Curl is a professor in, and chairman of, the department of chemistry. Smalley is the Gene and Norman Hackerman Professor of Chemistry and a professor of physics. For the past five years, he has also served as the chairman of the Rice Quantum Institute.



proposal, published in *Nature* in 1985, had made the quest one of the hottest in chemistry.

In our laboratory we collected the sooty carbon produced by the vaporization laser while using various chemical techniques to detect the presence of  $C_{60}$ . We shurried the soot in benzene, for example, and looked for a yellow color. But the solution in our test tubes stayed clear, with boring black soot sitting on the bottom. The community of cluster chemists ran many more sophisticated experiments but achieved no better result.

Many gave up hope of ever seeing the yellow vial. They reasoned that although the fullerenes may be stable, it was too hard to separate them from the other sooty material being produced in the vaporization experiments. Per-

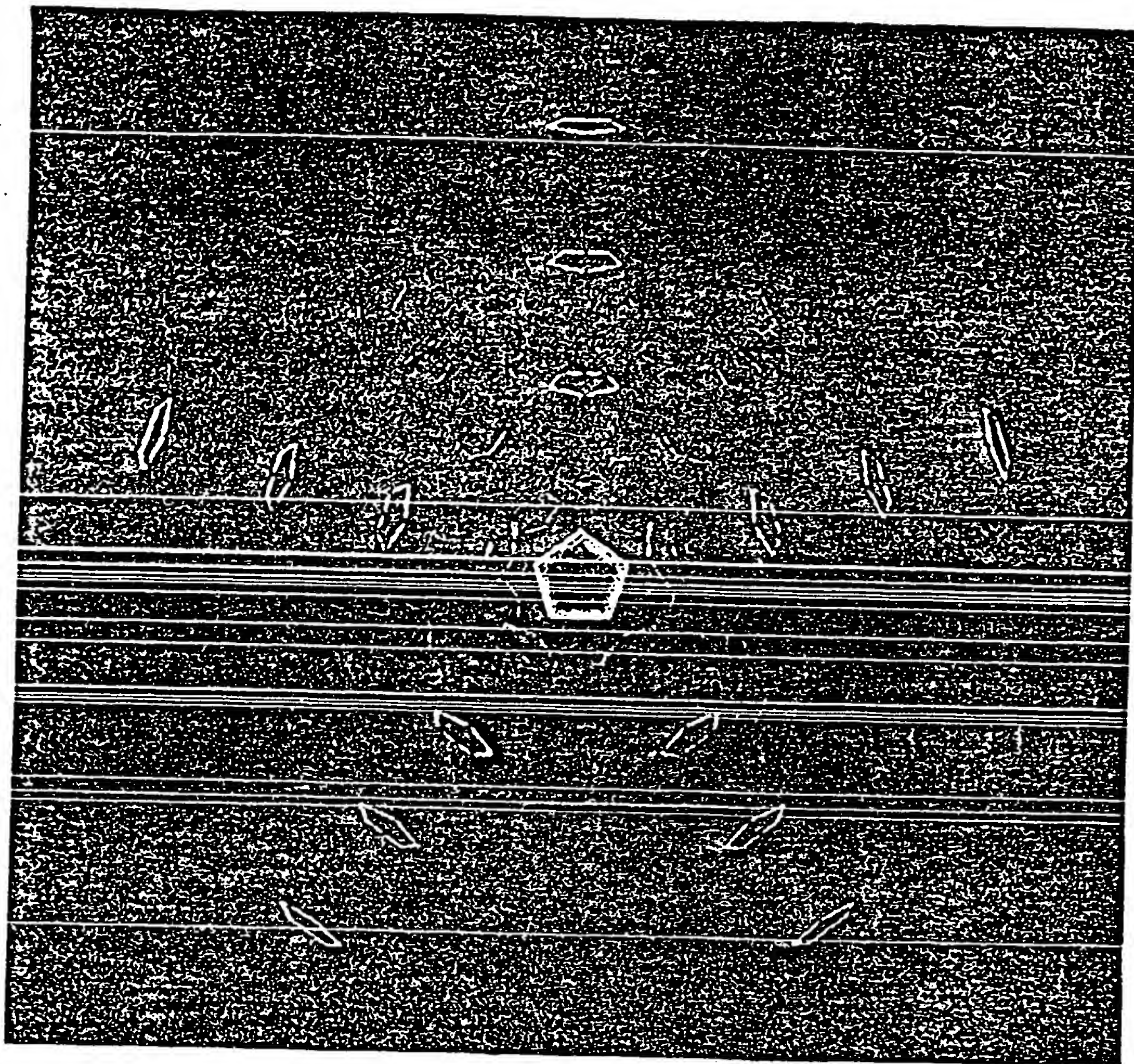
haps, the workers said, some dedicated chemist might one day extract a few micrograms with some special solvent, but no one seriously expected  $C_{60}$  to be available in bulk anytime soon.

In the end, the breakthrough was made not by chemists but by physicists working in a totally different area. Huffman, Krätschmer and their students had been engaged for decades in a study of interstellar dust, which they assumed to consist mainly of particles of carbon (the most common particle-forming element). They therefore modeled the phenomenon in the laboratory by vaporizing carbon and condensing it in as many ways as possible. Optical tests figured in most of the studies. (Virtually all that is known of the interstellar dust stems from obser-

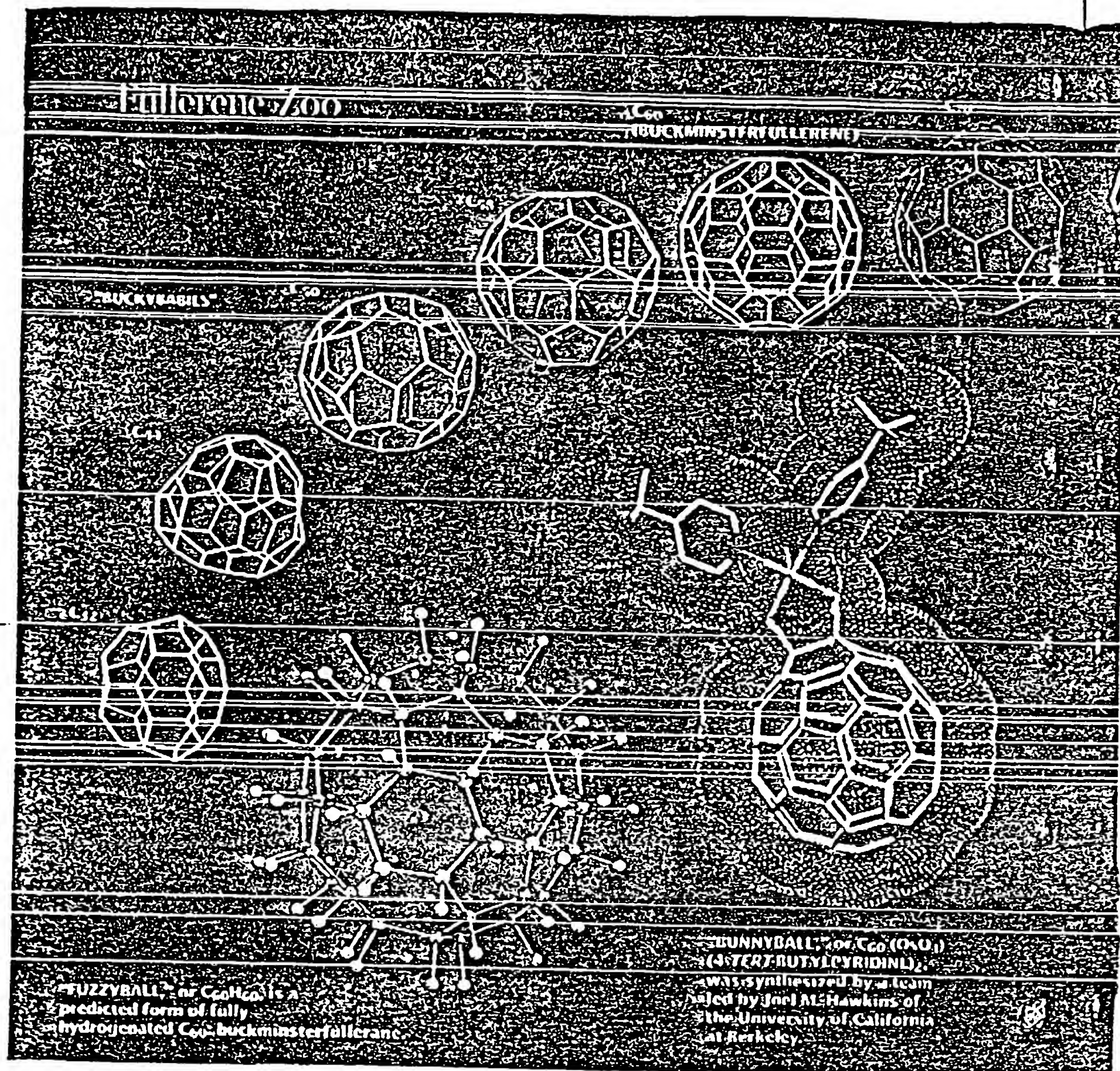
vations of how it absorbs and scatters starlight.)

In 1983 the physicists tried evaporating a graphite rod by resistive heating in an atmosphere of helium. They noticed that when the helium pressure was just right (about a seventh of an atmosphere), the dust strongly absorbed wavelengths in the far ultraviolet region, creating a peculiar, double-humped spectrum [see bottom illustration on page 58]. Most observers would have missed the two blips on the screen, but not Huffman and Krätschmer: they had studied spectra of carbon dust for years without encountering such an effect. They dubbed it their "camel" sample and wondered what it meant.

Nearly three years later, in the late fall of 1985, Huffman read in *Nature* of







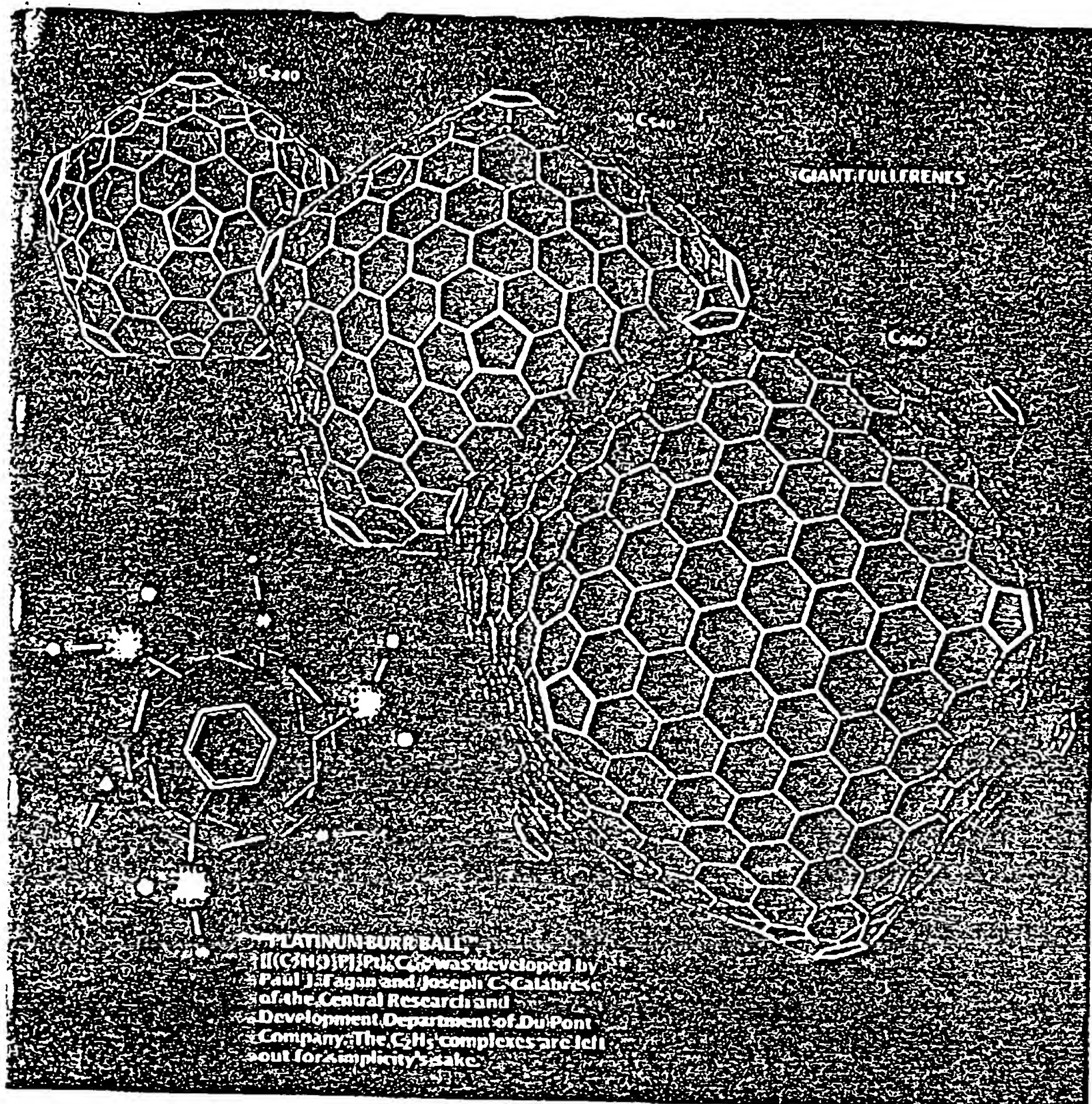
our discovery of  $C_{60}$  and began to wonder if a hollow soccerball molecule might be the cause of the double hump. Yet this explanation seemed too good to be true, for it required that  $C_{60}$  account for a significant portion of the sample. Why would so much of the carbon end up in such perfectly symmetric cages? What did the helium do to make it possible? The seeming unlikelihood of this hypothesis, together with some difficulty in reproducing the experiment, led the researchers to put the project on the back burner.

By 1989, however, Huffman and Krätschmer had become convinced that the  $C_{60}$  hypothesis ought to be reexamined. They renewed their interest in the camel sample, readily reproducing the results of the 1983 experiments. This time their attention turned to measuring the sample's absorption of infrared light—the wavelengths that interact with the vibrational motion of molecules—in order to test the results against theoretical predictions that had by now been made for soccerball  $C_{60}$ . These predictions held that of the 174

vibrational modes of this putative molecule, only 46 would be distinct, and only four would appear in the infrared range. To their surprise, they found the camel sample did display four sharp infrared absorption lines, and they verified that the lines were present only in carbon dust produced in the special camel way. This finding provided striking evidence that  $C_{60}$  might be present in abundance.

Influenced by their background in physics, the workers initially chose to test their hypothesis by a rather in-





involved route. They prepared a sample from pure  $^{13}C$ , a heavy isotope of carbon, and verified that the extra mass shifted the four infrared bands in the way expected for so large a molecule composed exclusively of carbon. Ultimately, however, they realized that the simplest assay followed a basic dictum of organic chemistry: like dissolves like. Should their sample dissolve in an aromatic solvent, such as benzene, this would support the predicted aromaticity of  $C_{60}$ . Because benzene molecules take the shape of a ring of carbon at-

oms,  $C_{60}$  would thus be seen as a kind of spherical benzene.

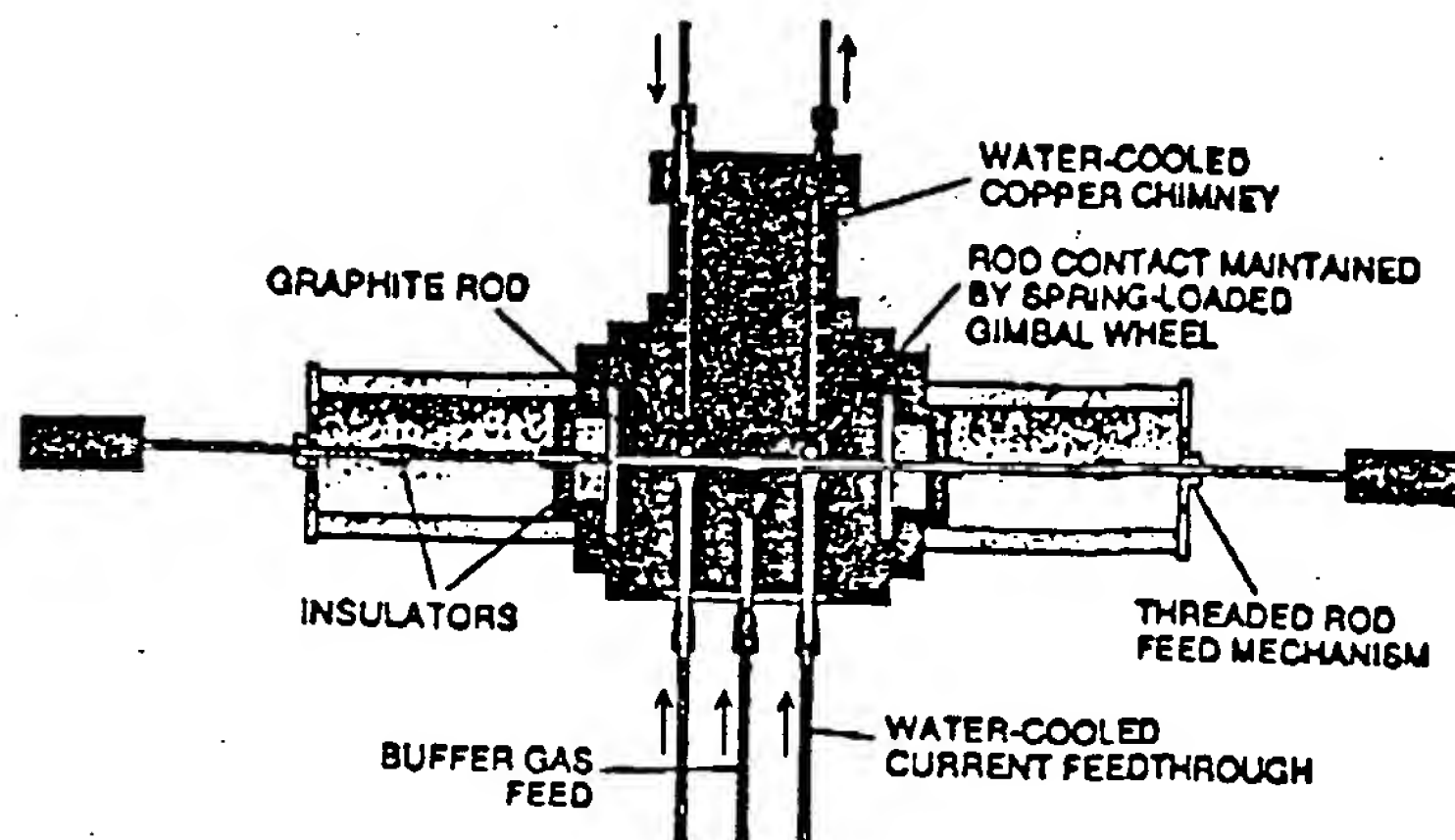
When the Kratschmer-Huffman group finally added benzene to their camel sample and saw the color red develop, they realized they were looking at the first concentrated solution of fullerenes ever seen. They evaporated the solvent and found that tiny crystals remained, which readily redissolved. These crystals could be sublimed under a vacuum near 400 degrees Celsius and condensed on a cold microscope slide to form smooth films of solid materials,

which Kratschmer and Huffman christened "fullerite."

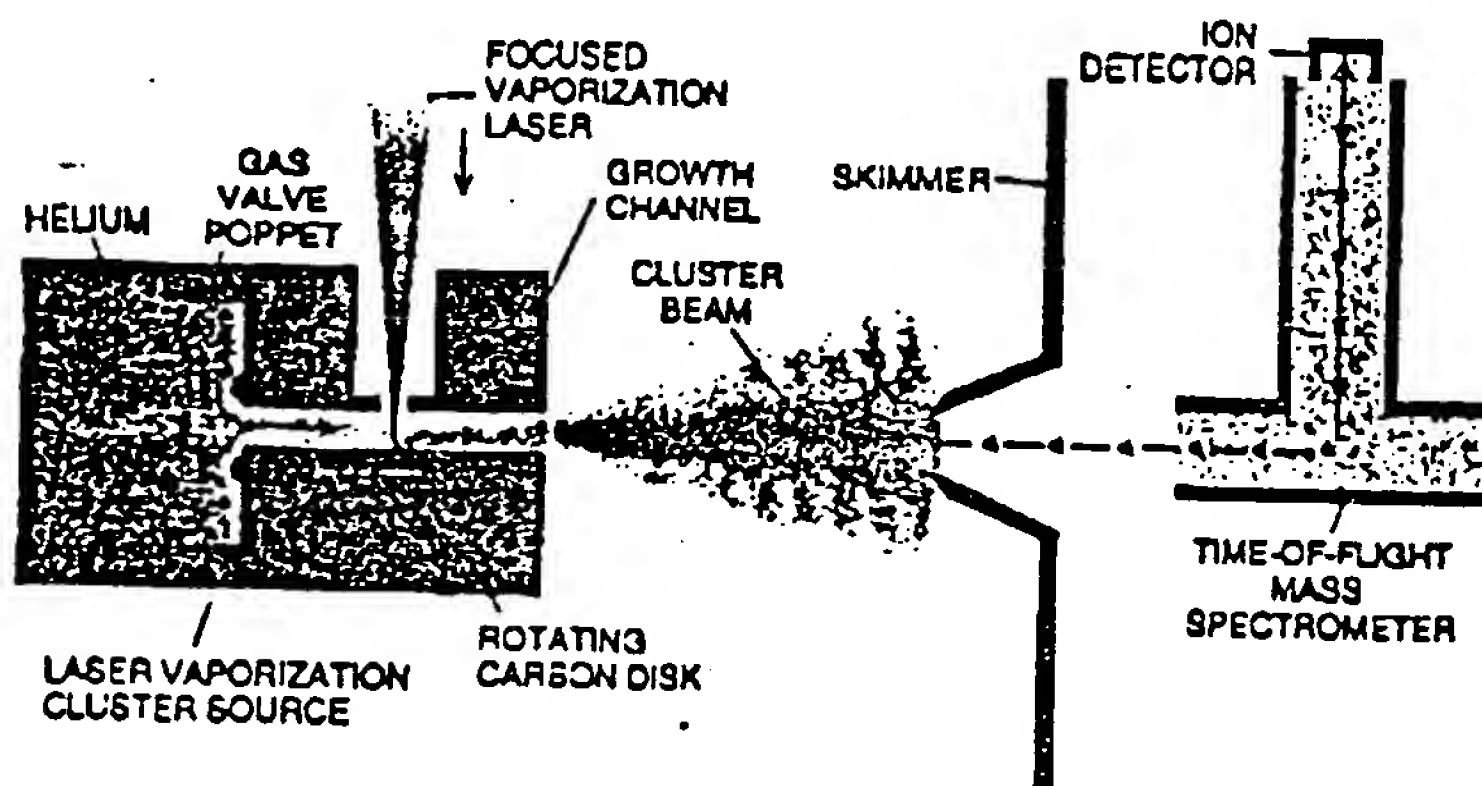
In thin layers these films were yellow (a fact that those of us at Rice University who searched for a "yellow vial" find highly gratifying). Although it took a while to obtain precise numbers, it is now known that carbon dust prepared in the camel way produces an extractable fullerene mixture made up of roughly 75 percent  $C_{60}$  (the soccer ball), 23 percent  $C_{70}$  (the rugby ball) and a grab bag of larger fullerenes.

Here was a new form of pure, solid

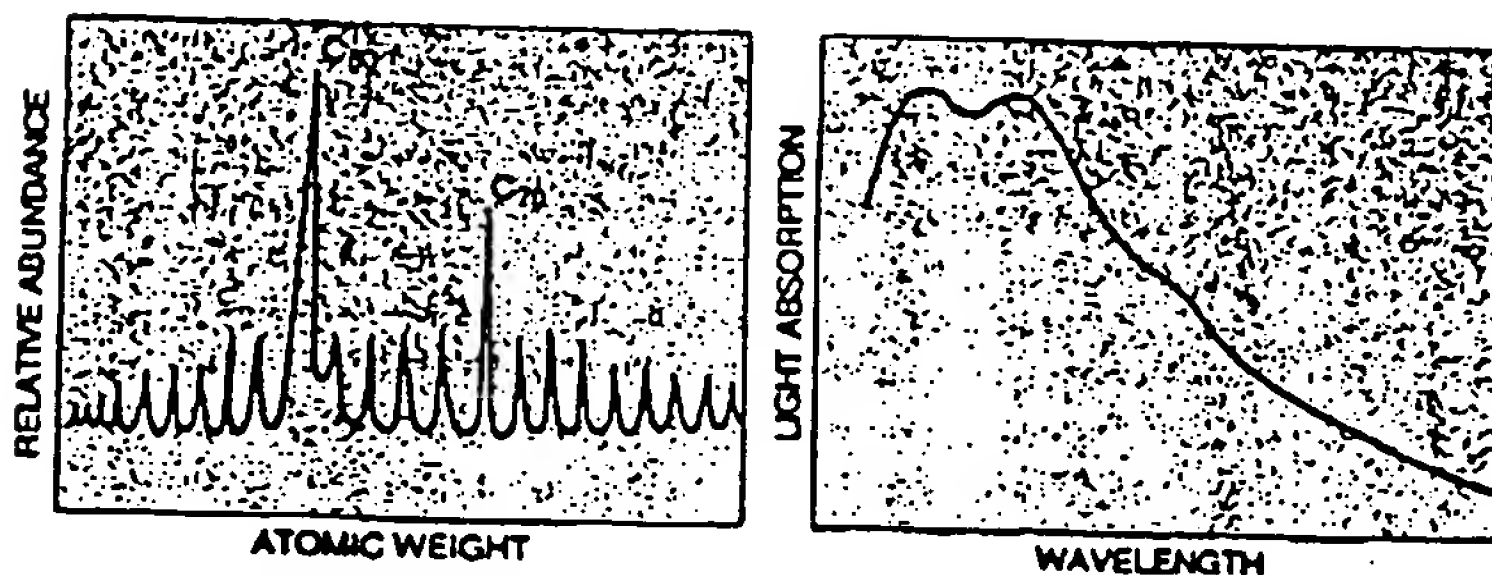




**FULLERENE FACTORY** makes macroscopic samples in a carbon arc. The arc—a refinement of an apparatus developed by Wolfgang Krätschmer and Donald Huffman—freezes carbon atoms that coalesce into sheets. Inert helium holds the sheets near the arc long enough for them to close in on themselves, forming fullerenes.



**CLUSTER GENERATOR** designed by one of the authors (Smalley) produced the first evidence that fullerenes can form from carbon vapor. A pulsed laser vaporizes carbon; a gust of helium then sweeps the vapor into a supersonic beam whose expansion cools the atoms, condensing them.



**CRUCIAL GRAPHS:** In 1985 the cluster-beam generator showed many even-numbered carbon clusters, especially  $C_{60}$ , suggesting that these species are particularly stable. The humped ultraviolet absorption spectrum led Krätschmer and Huffman to dub it the "camel" sample; in 1990 it was shown to contain  $C_{60}$ .

carbon. It is the only pure, finite form. The other two, diamond and graphite, are actually infinite network solids. In the real world, one usually deals with hunks of diamond cut out of larger bulk crystals. Under normal conditions, the surfaces of such a piece are instantly covered with hydrogen, which ties up the dangling surface bonds. Graphite is much the same. No piece of diamond, therefore, can ever be truly pure under normal conditions. The fullerenes, on the other hand, need no other atoms to satisfy their chemical bonding requirements on the surface. In this sense, the fullerenes are the first and only stable forms of pure, finite carbon.

Once the Krätschmer-Huffman results were announced at a conference in Konstanz, Germany, in early September 1990, the race was on. The study of  $C_{60}$  and the fullerenes had been the province of the few select groups that had something like our elaborate and expensive laser-vaporization cluster-beam apparatus. Now Krätschmer and Huffman had opened the field to anyone who could procure a thin rod of carbon, a cheap power supply, a bell-jar vacuum chamber and a few valves and gauges. Everybody could play.

Within a few months, many groups were making their own fullerenes. Physicists, chemists and materials scientists thus began an interdisciplinary feeding frenzy that continues to intensify as this article is being written [see box on page 62]. The key results have been quickly reproduced in over a dozen laboratories, some of which have applied alternative procedures of verification as well. Because fullerenes are readily soluble and vaporizable molecules that remain stable in air, they are perfectly suited to a wide range of techniques.

One of the most powerful techniques—nuclear magnetic resonance (NMR)—has confirmed the single most critical aspect of the soccerball structure: that all 60 carbon atoms have exactly the same relation to the whole. Only the truncated icosahedral structure we proposed for  $C_{60}$  arranges the atoms so symmetrically as to distribute the strain of closure equally. Such even distribution makes for great strength and stability. Indeed, that is why we proposed the structure in the first place: it explains the extraordinary stability of the 60-atom species.

Because  $C_{60}$  is the most symmetric molecule possible in three-dimensional Euclidean space, it is literally the roundest of round molecules. Edgeless, chargeless and unbound, the molecule spins freely, as NMR experiments show.

more than 100 million times a second. The NMR experiments also dramatically verify that  $C_{60}$  has the shape of a tiny rugby ball: at room temperature, it spins rapidly about its long axis, stopping its frantic motion only below the temperature of liquid air.

High-resolution electron microscopy revealed these little carbon balls one at a time—as predicted, they spanned a bit more than one nanometer (a billionth of a meter). Scanning tunneling microscopy showed that when  $C_{60}$  molecules are deposited on a crystalline surface, they pack as regularly as billiard balls. X-ray diffraction studies demonstrated that—as one would expect— $C_{60}$  crystallizes in a face-centered cubic lattice, with the balls a little more than 10 angstroms apart [see illustration on page 62]. The crystals are as soft as graphite. When squeezed to less than 70 percent of their initial volume, calculations predict that they will become even harder than diamond. When the pressure is relieved, they are observed to spring back to their normal volume. Thrown against steel surfaces at speeds somewhat greater than 17,000 miles per hour (about the orbital speed of the U.S. space shuttle), they are incredibly resilient: they just bounce back.

We found that the most convenient way to generate fullerenes consists of setting up an arc between two graphite electrodes. We maintained a constant gap by screwing the electrodes toward each other as fast as their tips evaporated. The process worked best when the helium pressure was optimized and other gases, such as hydrogen and water vapor, were rigorously eliminated. Such measures produced yields of dissolvable fullerenes that typically ranged between 10 and 20 percent of the vaporized carbon. Yields as high as 45 percent have recently been reported.

The only irreducible cost appears to be that of the electricity needed to run the arc. But even the small bench-top generators we are now using in our laboratory provide electricity at a cost that amounts to only about five cents per gram of  $C_{60}$ . Recently it has been found that a sooting flame (such as that of a candle) can be used to produce substantial yields of  $C_{60}$ . In the long run, this may prove the cheapest way to make the material. When the first large-scale applications of fullerenes are found—perhaps in superconductors, batteries or microelectronics [see box on page 62]—the manufacturing cost of  $C_{60}$  will probably fall close to that of aluminum: a few dollars a pound. What had recently been described as the "most controversial molecule in the

Cosmos" is well on its way to becoming a bulk commodity.

A host of questions arises out of this wonder. What exactly is the helium doing? How can such a perfectly symmetric molecule be formed with such high efficiency out of the chaos of a carbon arc? And, on a more personal level, where did we go wrong? Why did we, and all other chemists for that matter, fall in the search for the yellow vat? Our technique involved helium as well. What did the Krätschmer-Huffman team do that made such a big difference?

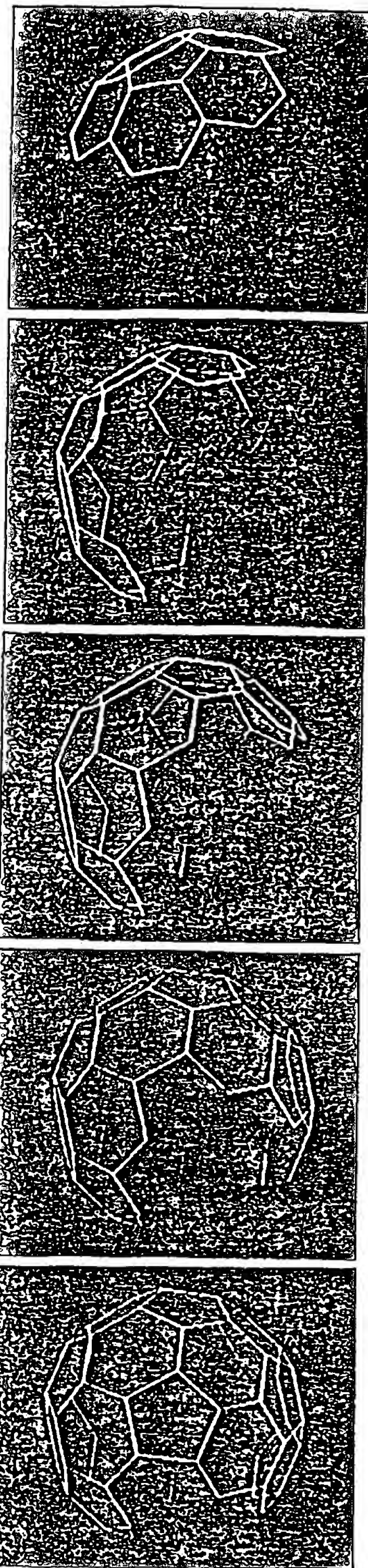
We now believe the answers to these questions lie in the way carbon vapor condenses at high temperatures. Linear carbon chains appear to link together to form graphitic sheets, and the sheets anneal as they grow in the hot vapor. Finally, stable, cage-like structures are favored by a key concept, which we call the pentagon rule.

Scientists had long known that when carbon is vaporized, most of its atoms initially coalesce into clusters ranging from two to 15 atoms or so. The very smallest carbon molecules are known to prefer essentially one-dimensional geometries. But clusters containing at least 10 atoms most commonly form a monocyclic ring—a kind of molecular Hula-Hoop that is especially favored at low temperatures. At very high temperatures, the rings break open to form units that comprise as many as 25 carbon atoms, taking the form of linear chains. Such chains might be imagined to look something like writhing snakes as they vibrate in the hot vapor.

It was these linear carbon chains that initially got us involved in carbon cluster studies and led to the discovery of  $C_{60}$ . Our British colleague, Harry Kroto, had theorized that the great abundance of such linear carbon chains in interstellar space may arise from chemical reactions in the outer atmospheres of carbon-rich red giant stars. In the early 1980s one of us (Smalley) had developed a supersonic cluster-beam device for the general study of small clusters composed of essentially any element in the periodic table [see "Microclusters," by Michael A. Duncan and Dennis H. Rouvray; SCIENTIFIC AMERICAN, December 1989].

We produced clusters by focusing an intense pulsed laser on a solid disk of the element to be studied. The local temperature could readily be brought above 10,000 degrees C—hotter than the surface of most stars and certainly hot enough to vaporize any known material. The resulting vapor was entrained in a powerful gust of helium, a chemi-

## Growth of a Buckyball





cally inert carrier gas, which cooled the vapor so that it could condense into small clusters. As the carrier gas expanded through a nozzle into a vacuum, it generated a supersonic beam of clusters whose sizes could be measured by a mass spectrometer.

In 1984 a group at Exxon using a copy of the cluster-beam apparatus developed at Rice had been the first to study carbon clusters in this fashion. Their results strongly suggested that the linear carbon chains Kroto wanted to study were in fact being produced in abundance. In addition, they reported a bizarre pattern among the larger clusters: the distribution was strikingly lacking in the species having an odd number of atoms.

The Exxon researchers recorded but did not notice that two particular even-numbered members,  $C_{60}$  and  $C_{70}$ , were somewhat more abundant than their neighbors [see bottom illustration on page 58]. The mysterious even-numbered distribution of clusters was separated from the small linear-chain distribution by what appeared to be something of a forbidden zone—a region of clusters between roughly 25 and 35 atoms in size in which few if any clusters could be detected.

The even-numbered distribution was soon discovered to result from the fullerenes. In one of our many studies of Kroto's linear carbon chains, we reproduced the Exxon results but found something quite striking about the distribution of large, even-numbered clusters. Heath, Kroto and O'Brien noticed that the 60th cluster seemed five times more abundant than any other even-numbered cluster in the range between 50 and 70 atoms. This differential was dramatically greater than anything that had been seen before.

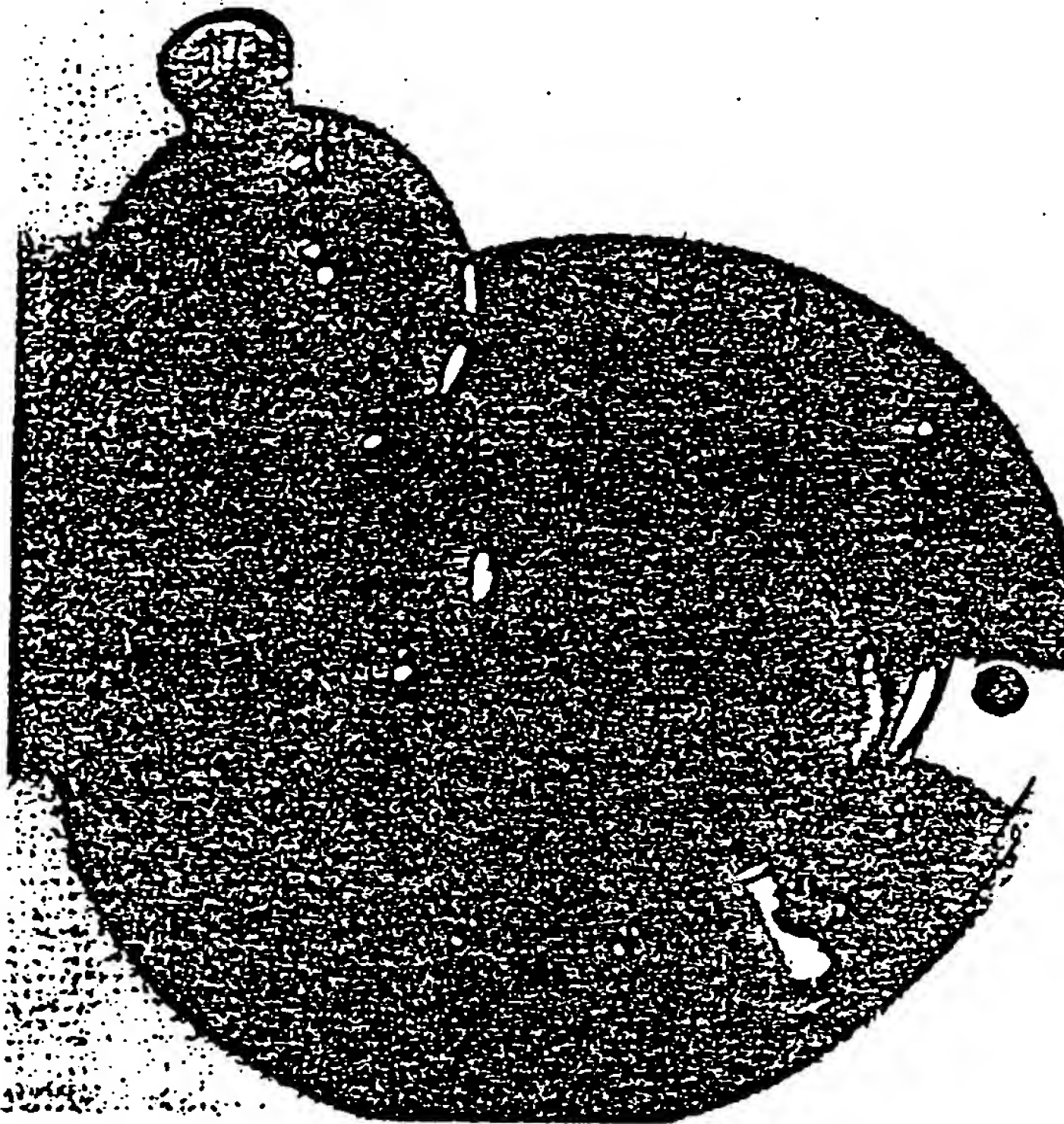
After much discussion, Heath and O'Brien spent the next weekend playing with the conditions in the laser-vaporization machine's supersonic nozzle. By Monday morning they had managed to find conditions in which  $C_{60}$  stood out in the cluster distribution like a flagpole. By the next morning we had had our Eureka! experience, and we were playing with every sort of soccerball we could get our hands on.

We found that we could explain the dominance of the even-numbered clusters by assuming they had all taken the structure of hollow, geodesic domes. They were all fullerenes. We could also argue that some fullerenes were more abundant than others because of the smoothness of the clusters' surface and the natural grouping of pentagons.

Pentagons provided an important clue. Although hundreds of examples are known in chemistry of five-membered rings attached to six-membered rings in stable aromatic compounds (for example, the nucleic acids adenine and guanine), only a few occur whose two five-membered rings share an edge. Interestingly, the smallest fullerene in which pentagons need not share an edge is  $C_{60}$ ; the next is  $C_{70}$ . Although  $C_{70}$  and all larger fullerenes can easily adopt structures in which the five-membered rings are well separated, one finds that these pentagons in the larger fullerenes occupy strained positions.

This vulnerability makes the carbon atoms at such sites particularly susceptible to chemical attack.

The big question, however, was not why fullerenes were stable but rather how they formed so readily in laser-vaporized graphite. Near the end of 1985, we suggested that the process began with linear chains. As the carbon vapor began to condense, the linear chains would grow long enough to flip back on themselves to form large monocyclic Hula-Hoops. As the growth continued, the chains would also fold into more effectively connected polycyclic network structures. Because graphite,



COLOR OF  $C_{60}$  depends on its form. This yellow film was sublimed onto a glass window that had been bolted to a vacuum oven. The benzene solution is magenta.



FULLERENE CRYSTALS were produced by evaporating a benzene solution of  $C_{60}$  containing a significant admixture of  $C_{70}$ .



the most stable known form of carbon, has its atoms bound in infinite hexagonal sheets, we suspected that the polycyclic network clusters resembled pieces of such sheets. We expected it to look like a fragment of chicken wire.

Like a cutout section of chicken wire,

these graphitic sheets would have many dangling bonds, making them chemically reactive—much more so than the smaller linear chains, which have only two such bonds, one on each end. The sheets, therefore, would not be expected to be abundant in the cluster beams.

Almost as soon as they form, they react with other small carbon molecules and grow too large to be seen. This, we believe, explains why there is a forbidden zone between the small linear-chain distribution and the first small fullerenes. Chemists are conditioned to think of

## Fullerene Electronics

Currently the most technologically interesting properties of bulk  $C_{60}$  are electronic: in various compound forms it functions as an insulator, a conductor, a semiconductor and a superconductor.

The material crystallizes when  $C_{60}$  molecules pack together like Ping-Pong balls in a face-centered cubic lattice. Calculations over the past few months have predicted that this new material is a direct band-gap semiconductor like gallium arsenide. All its units stand precisely at their posts in a crystalline structure. But unlike the elements of gallium arsenide, the buckyballs spin freely and at random. This disorder gives them a certain resemblance to amorphous silicon—a constituent of inexpensive solar cells. The peculiar disorder within order of bulk  $C_{60}$  has yet to be fully explored, but it is expected to produce a wholly new kind of semiconductor.

Early in 1991 researchers at AT&T Bell Laboratories discovered that they could mix, or dope,  $C_{60}$  with potassium to produce a new metallic phase—a "buckide" salt. It reaches its maximum electrical conductivity when there are three potassium atoms to each buckyball. If too much potassium is added, however, the material becomes insulating. Subsequent work has shown that  $K_3C_{60}$  is a stable metallic crystal consisting of a face-centered cubic structure of buckyballs, with potassium ions filling the cavities between the balls. Potassium buckide is the first completely three-dimensional molecular metal.

The Bell Labs team further discovered that this  $K_3C_{60}$  metal becomes a superconductor when cooled below 18 kelvins. When rubidium is substituted for the potassium, the critical temperature for superconductivity was found to be near 30 kelvins. (Recently workers at Allied-Signal, Inc., detected superconductivity at 43 kelvins for rubidium-thallium-doped material.) Careful work at the University of California at Los Angeles has shown that the superconducting phase is stable and readily annealed—imperfections can be smoothed away by heating and cooling.

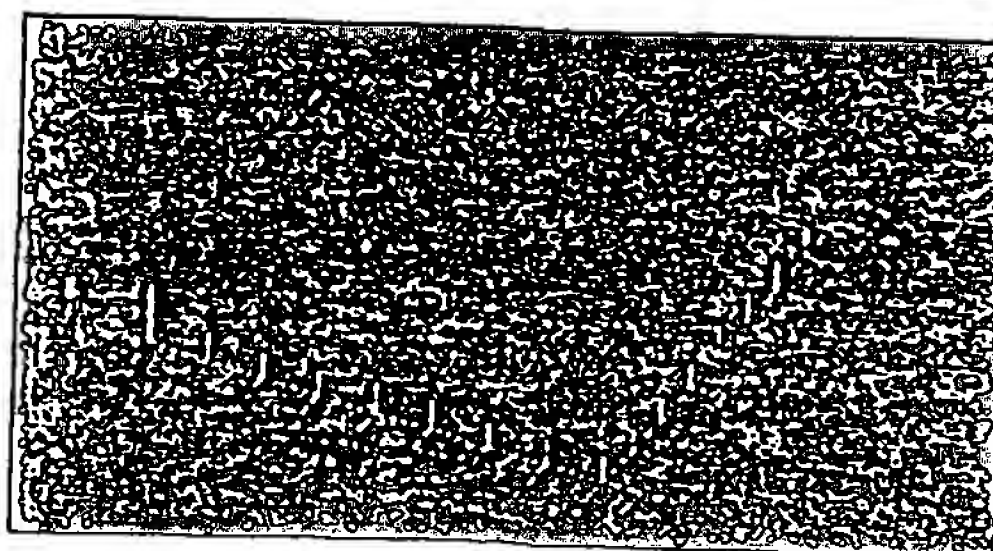
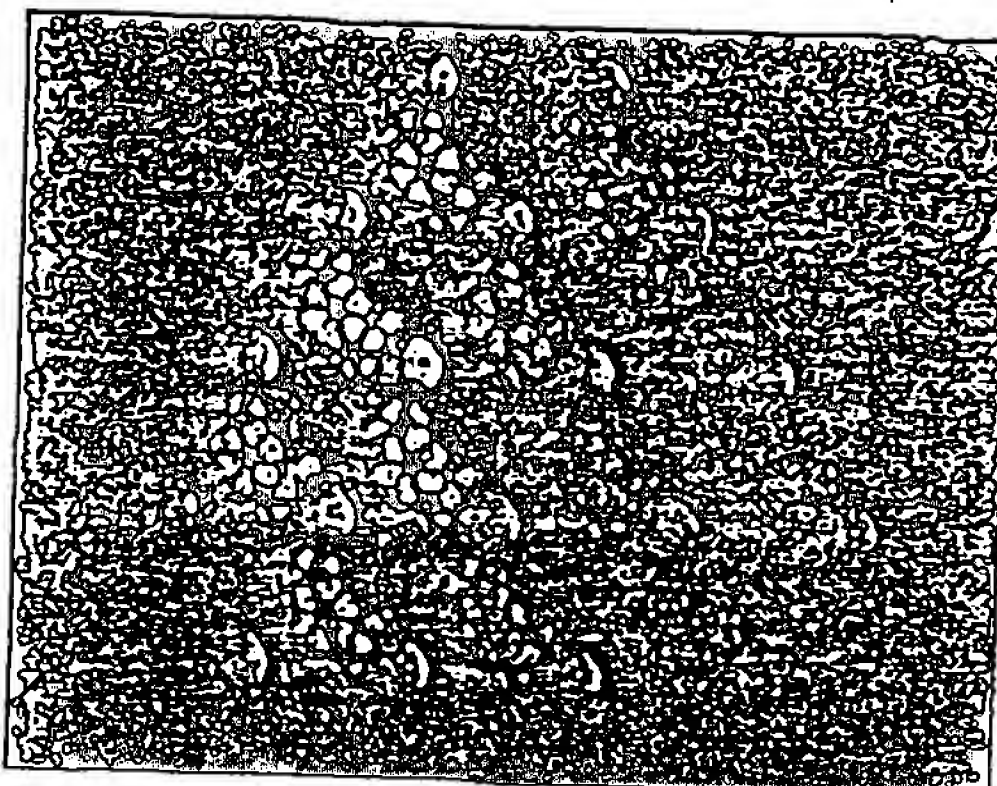
The material can therefore be manufactured as a three-dimensional superconductor, making it a candidate for practical superconducting wires. Early estimates of magnetic and other characteristics indicate that these superconducting buckide salts are similar to the high-temperature superconducting ceramics made of yttrium, barium and copper oxide.

Recent work at the University of Minnesota has shown that highly ordered  $C_{60}$  films can readily be grown on crystalline substrates, such as gallium arsenide. This attribute makes the film a suitable material for microelectronic fabrication. Beautifully regular films of the  $K_3C_{60}$  superconductor can also be made [see micrograph at right], and the interface between the  $C_{60}$  crystalline film and the  $K_3C_{60}$  material has been found to be stable. It may thus lend itself to the production of intricately layered microelectronic devices.

In order for the semiconducting properties of fullerene materials to be thoroughly exploited, scientists need to

learn how to dope them selectively to make *n*-type and *p*-type fullerene films, which donate electrons and holes, respectively. Such doping may involve putting a dopant atom inside the cage, either by growing the cage around the atom or by shooting atoms through the carbon walls by brute force. Small atoms, such as helium, have already been injected this way into the  $C_{60}$  cage, and it seems likely that hydrogen and lithium are insertable as well.

The versatility of bulk  $C_{60}$  seems to grow week by week. As we go to press, for example, there is a report suggesting that fullerene complexes exhibit ferromagnetic qualities in the absence of metals, an unparalleled phenomenon. Also, British workers from the universities of Leicester, Southampton and Sussex have just reported the generation of macroscopic quantities of fully fluorinated buckyballs ( $C_{60}F_{60}$ ). The resulting "teflon balls" may be among the world's best lubricants. We do not know what the fullerenes' burgeoning traits will allow, but it would be surprising if the possibilities are not wonderful.



SUPERCONDUCTING FULLERIDE forms when buckyballs are doped with potassium in the ratio of  $K_3C_{60}$  (diagram), producing a crystal that can be grown on a gallium arsenide substrate (scanning tunneling micrograph).

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